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A NEW CALORIMETER BOMB WITH SPECIAL ADVANTAGES AS TO MATERIAL OF CONSTRUCTION AND METHOD OF OPERATION.[1]

By S. W. Parr.

In attempting to improve upon the oxygen bomb for calorimetric use, the efforts have been directed along two distinct lines to meet what seemed to be the most pressing needs of the case: *first*, the discovery of some substitute for platinum which would resist the corrosive action of the acids formed and, *second*, the improvement of the methods for closing the receptacle so that a perfect seal could be secured with certainty and ease.

With reference to the first item, the development of a substitute for platinum, the problem is not without serious difficulties. It is to be borne in mind that in many instances, as with coals and similarly constituted substances, the nitric acid resulting from the combustion is produced under the best possible conditions for promoting a solvent action. The concentration of the acid in the bomb after a reaction is considerable. Moreover, the temperature, at least for a short period, is relatively high and the presence of corroding gases under high pressure may contribute to the activity. Again, in many substances a high percentage of sulphur exists and this burns to SO_3 or in the atmosphere of the interior, saturated as it is with water vapor, to H_2SO_4. For example, a very large part of the coals of the Mississippi valley have a content of sulphur amounting to 3 or 4 per cent. of the gross weight of the coal. Indeed, a content of sulphur is not infrequently met with of five and even six per cent. We have then in these cases of common occurrence conditions wherein both sulphuric and nitric acids are formed and these of a rather concentrated character. One of the common methods of counteracting the action of the acids is by use of some sort of resistant covering. As will be seen later, the method devised for closing the bomb involves the machining of the parts of dimensions accurate within $^1/_{50}$ of a millimeter. This feature, therefore, would make it impracticable to make use of an enamel as a protective covering. This expedient is also found, in

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[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

practice, to be objectionable, owing to the frequent ruptures that are certain to occur in the enameled surface, thereby admitting the acid to the metal beneath. So far as a platinum lining is concerned in the device contemplated, and this was given an extended trial, the difficulties were as follows: First, the cost of platinum, representing at the current prices approximately $400 per bomb, made the use of that metal prohibitive, especially where a considerable number of bombs were desired such as for use with large classes. Second, the method of closing the bomb called for an exact relationship as to dimensions, and, as in the case of enameling, this could not easily be secured or maintained with an inner shell or lining. Moreover, the device to be employed for the inlet valve was such as to make it a very difficult problem of construction to make use of a second metal in that part of the apparatus. Third, the inevitable corrosion which sooner or later begins under the platinum shell roughens the surfaces, especially those coming in contact with the gasket. In time the entire surface under the platinum is affected and the water equivalent as well as the strength of the bomb is modified. These reasons alone, even if there were no others, are quite sufficient for indicating that the bomb, if made at all in conformity with the design contemplated, should be made of a metal capable of being machined to exact dimensions and in conformity with a desired pattern.

For this purpose, therefore, a study of alloys was undertaken with a view to determining if one could be devised sufficiently resistant to acid to effectually replace platinum, and that at the cost in the massive form necessary to easily compete with that metal. It must be possible, moreover, to either cast or stamp the metal into proper form suitable for machining into the final and exact shapes desired. The alloy finally developed has proved to be eminently satisfactory as far as its acid-resisting properties and strength are concerned. It is complex in composition, having as the chief components nickel, copper, tungsten and chromium with smaller and more or less adventitious amounts of manganese, aluminum, titanium, boron and silicon. The details of composition and properties of the alloy as finally adopted are presented under another title.[1] Concerning the securing of this material in forms suitable for machining to the desired patterns, only the method of melting and casting has so far been undertaken. The difficulty of securing perfect castings has seemed at times almost insurmountable. This is due to the fact that the melting point of the alloy is relatively high, approximately 1300°, and at the point of solidification the shrinkage is so great that cracks or flaws are opened up which render the casting unfit for use. Again, the occlusion of gases at the high melting temperature is great and pin holes are apt to be a source of much annoyance. The overcoming of these difficulties is, however, a mechanical rather than a chemical problem and need not be entered into here.

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[1] "A New Alloy with Acid-Resisting Properties," by S. W. Parr, Inorganic Section (Sec. II) this Congress.

That the material may fairly be considered a substitute for platinum in the service here described is shown in the article above referred to, wherein is given a table of solubility tests. Also in another article accompanying this discussion[1] data are given upon a bomb of this new material in practical operation, which indicate that the alloy is entirely suited for use in the manner described.

The second improvement sought for relates to the method of closing the receptacle. The difficulties attending the use of lead gaskets relate chiefly to the stress and strain required to secure a perfect seal. Other objections relate to the chemical action upon the lead, and to the pitting or corrosion of the needle valve or seat, making it necessary to frequently reseat or repoint the valve parts. The substitution of rubber for lead is found to be entirely practicable if the conditions under which it is used are such that flame or any of the processes of combustion are not allowed to come in contact with the rubber. This is easily accomplished by interposing between the rubber gasket and the inner chamber a shoulder of massive metal so constructed that the cross section of the space between the two metallic parts is so small, say $^1/_{25}$ of a millimeter, and the longitudinal measurement of the space, that is the distance from the rubber to the inner chamber, is so great, say $1^1/_2$ or 2 millimeters, that the combustion processes may not travel along so narrow a passage and therefore do not come in contact with the rubber gasket. This principle is carried out in closing the main opening of the bomb and also in closing the valve through which oxygen is admitted. This will be made clear by reference to a sketch.

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[1] "Some Tests on a New Calorimeter Bomb," by Richard H. Jesse, Jr., THIS JOURNAL, p. 748.

In Fig. 1, *B B* are the walls of the bomb which enclose the space *O*. The cover *C* is made with an encircling rim, *R*, which retains the rubber gasket *G*. The cover is so made that a shoulder. *S S*, passes the wall of the bomb as it comes up to position against the gasket. The machining of the parts is such that the space between the shoulder and the wall is about $^{1}/_{25}$ mm. Moreover, the distance from the lower edge of the shoulder to the gasket is about 2 mm. This is increased slightly by the pressure of the cover upon the gasket when the screw cap is brought down upon it. Conditions are thus secured which prevent the traveling of flame or any of the processes of combustion from the combustion chamber *O* to the rubber gasket *G*. The same principle is observed in the arrangements for the inlet valve *V*. The small gasket *g* is protected from the reactions or heat of the combustion chamber by narrow passages between metal walls.

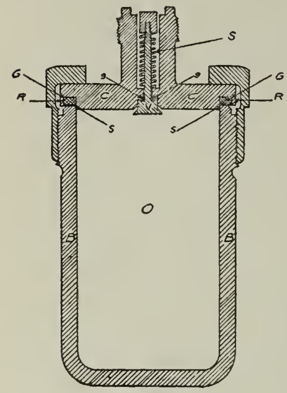

Fig. 1.

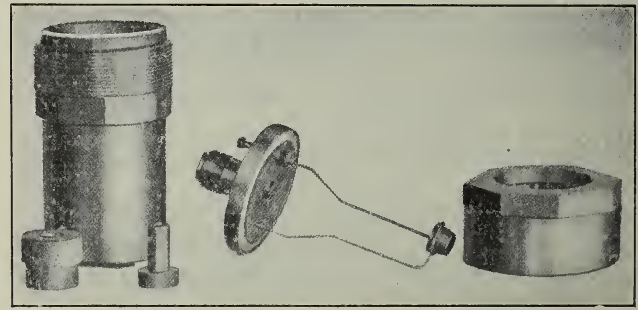

Fig. 2.

In this manner it is entirely possible to secure a perfect seal with a minimum amount of compression, by use of rubber gaskets and this without any burning whatever of the rubber.

A word further as to convenience of operation. The valve *V* works automatically thus: The valve is held lightly in place by the springs, but upon the admission of the oxygen above the valve it is forced downward admitting the gas to the chamber *O*. When the proper amount is admitted, say 25 atmospheres, the oxygen supply is shut off and immediately the valve is lifted into place by the spring. The strong pressure from within tends to seat the valve more

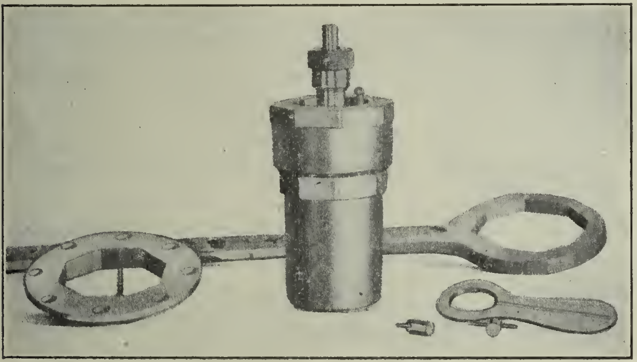

FIG. 3.

firmly in place. After an extended experience with this type of valve, involving numerous modifications, the present form shown herewith has been found to be exceedingly effective and satisfactory. Thumb pressure on the top of the stem is found sufficient for releasing the gas at the close of an experiment. The most striking characteristic, however, in the manipulation of the bomb is the ease with which the cover may be fastened to withstand the necessary pressure without leakage. As may be seen in the accompanying illustrations, a simple octagon plate is set into the table or shelf and an octagon wrench about 50

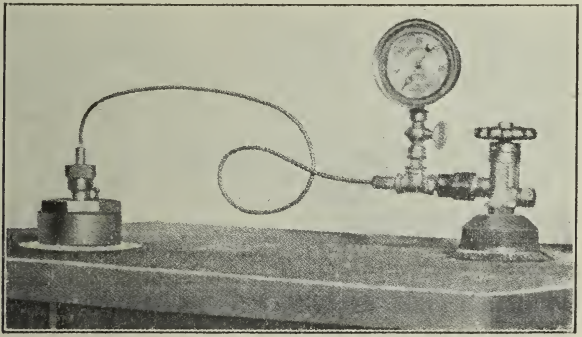

FIG. 4.

cm. long affords ample leverage for screwing down the cap and seating the cover. The expenditure of a great amount of force in this part of the procedure is quite eliminated. The ease and readiness with which a perfect seal can thus be obtained have done much to revolutionize the work of operating a calorimeter of the oxygen bomb type.

Fig. 2 shows the cover and screw cap removed from the bomb. The small parts at the base of the bomb are couplings for oxygen connection at the top of the cover.

Fig. 3 shows the bomb with the parts assembled with the octagon holder and wrench for setting the screw cap.

Fig. 4 shows the shelf fittings and connection with the oxygen tank. The shelf is hinged at the left-hand edge. It may be unfastened at the right-hand edge and lifted for the removal of the tank when it is required to renew the supply of oxygen.

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SOME TESTS ON A NEW CALORIMETER BOMB.[1]

By Richard H. Jesse, Jr.

In connection with the preceding description of the new alloy bomb of nickel-copper-chromium[2] it may be of interest to report briefly the results of a series of experiments on the combustion of two standard substances, cane sugar and benzoic acid. These experiments were undertaken not only for the purpose of standardization but also to test the behavior of the instrument under actual working conditions.

The principal features of difference between this bomb and other types are: (1) the substitution of an alloy, very resistant to the action of acids, for the usual platinum, gold, or enamel lining; (2) the use of a well protected rubber gasket for sealing the bomb instead of a gasket of lead; (3) the replacement of the ordinary steel needle-valve by a seated valve bearing a rubber gasket. For one who has spent much physical and mental effort in trying to seal completely bombs fitted with needle valves and gaskets of lead and gold, a very short experience is sufficient proof of the superiority of the present method of sealing in so far as speed and ease of manipulation are concerned. Former experience in this laboratory has offered evidence that these features do not cause a decrease in the accuracy desired for commercial fuel analysis. It has remained, however, to prove that they will answer the purposes of investigations where the highest attainable accuracy is desired.

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[1] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] This bomb was devised by Professor S. W. Parr, of this laboratory, and is described in the preceding paper.

A series of semi-quantitative corrosion tests in which specimens of the alloy were exposed at ordinary temperatures and for varying lengths of time to the action of 4 *N* sulphuric and nitric acids and mixtures of the two have indicated that the amounts of alloy which would dissolve in the time of a determination are negligible. To test the corrosion under working conditions, the washings from eight runs, which had been titrated in the usual manner for nitric acid with potassium hydroxide, were combined and analyzed for copper and nickel. The copper was precipitated by hydrogen sulphide in acid solution and was weighed as cuprous sulphide; the nickel was determined by the dimethylglyoxime method. In the eight determinations 1.6 milligrams of copper and 6.2 milligrams of nickel were dissolved. In a single determination therefore we have the solution of 0.2 mg. Cu and 0.8 mg. Ni. The quantity of the metal nitrates would have a heat of formation of approximately 1.8 calories.[1]

Since in these experiments the total amount of heat measured in a run was 9500 calories, about 0.02 per cent. of the rise was due to the solution of the alloy. This is a quantity which cannot be directed with certainty even in the very best calorimetric work. This particular bomb was the first successful casting. Since the work was begun, there have been slight modifications in the composition of the alloy which have probably increased its acid resistance. Quantitative evidence on this point is, however, lacking as yet. In coal calorimetry, sulphuric acid will be present in addition to the nitric acid. The corrosion tests already mentioned show that the mixture of these two acids is not much more active than nitric acid alone.

There is only indirect proof to show that the use of rubber gaskets is without effect on the accuracy of the bomb. The construction of the instrument is such that the rubber is well protected. The portion of the gasket which comes in contact with the gases in the bomb is a ring about $^1/_{1000}$ inch in width; to reach this the hot gases have to pass through a very narrow space with massive metal on each side so that they would almost certainly be cooled below the danger point. In these experiments there was absolutely no smell of burnt rubber in the bomb after a combustion. The constancy of the results given below is further proof that the rubber has no harmful effect, because it is hardly conceivable that if the rubber were burnt at all it should be burnt in such constant amount each time.

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[1] Thomsen's results in Landolt-Börnstein:

$\mathrm{Ni} + 2\mathrm{N} + 60 + \mathrm{Aq} = \mathrm{Ni(NO_3)_2Aq} + 113{,}200$ cal.

$\mathrm{Cu} + 2\mathrm{N} + 60 + 6\mathrm{H_2O} = \mathrm{Cu(NO_2)_2}.\ 6\mathrm{H_2O} + 92{,}900$ cal.

The method of adiabatic calorimetry[1] devised by T. W. Richards was used for these combustions.

The principle of the method is that the calorimeter is surrounded on all sides and on top by a bath of caustic soda, the temperature of which is at all times kept the same as that of the calorimeter. By running in sulphuric acid in measured amounts the temperature of the bath can be readily changed so that it conforms to that of the calorimeter even during the first rapid rise. This method has already proved itself capable of extreme accuracy. The mercury thermometer used was of the Beckmann type and was calibrated by the Bureau of Standards. The results with it were very satisfactory. Three different samples of sugar were used. They were supplied at different times during the past three years by the Bureau of Standards. Two samples of benzoic acid were burnt, one from the Bureau of Standards and one that had been carefully purified in this laboratory; experiment marked No. 10 was on the latter sample. The agreement is all that could be desired.

All the experiments fell within the temperature range 21–25° C. Since the temperature rise measured was about 3°, it follows that the mean temperature of any experiment did not differ from that of any other by more than 1°. This is worthy of mention because in this neighborhood the heat capacity of water changes by about 0.02 per cent. per degree. However, since the metal portions of the system have a larger temperature coëfficient of opposite sign, the

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[1] *Proc. Amer. Acad.*, **42**, 573 (1907); *Z. physik. Chem.*, **59**, 532; *J. Am. Chem. Soc.*, **32**, 431 (1910).

CANE SUGAR.

No.	Weight substance in air. Grams.	Observed rise corrected for bore protruding thread and stirring.	Correction for iron wire burnt.	Correction for HNO_3 formed.	Corrected rise.	Rise per gram substance.	Deviation from mean. Per cent.
1	2.4994	2.909°	—0.008°	—0.003°	2.898+°	1.1596°	+0.05
2	2.5018	2.908	—0.006	—0.004	2.898+	1.1585	—0.05
3	2.4987	2.910	—0.008	—0.004	2.898—	1.1597	+0.06
4	2.5004	2.909	—0.006	—0.004	2.899—	1.1593	+0.02
5	2.5035	.911	—0.008	—0.003	2.900	1.1583	—0.07
6	2.2743	2.646	—0.007	—0.003	2.636	1.1590	0.00

Average rise per gram sugar (weighed in air) = 1.1591°.
Average rise per gram sugar (weighed in vacuum) = 1.1584°.

BENZOIC ACID.

No.	Weight substance in air. Grams.	Observed rise corrected for bore protruding thread and stirring.	Correction for iron wire burnt.	Correction for HNO_3 formed.	Corrected rise.	Rise per gram substance.	Deviation from mean. Per cent.
7	1.5089	2.812°	—0.007°	—0.003°	2.802°	1.8570°	+0.02
8	1.5390	2.870	—0.008	—0.004	2.858	1.8570	+0.02
9	1.5059	2.809	—0.008	—0.004	2.797	1.8574	+0.04
10	1.4467	2.698	—0.008	—0.003	2.687	1.8572	+0.03
11	1.5635	2.913	—0.008	—0.003	2.902	1.8561	—0.04
12	1.5630	2.912	—0.007	—0.004	2.901	1.8560	—0.04
13	1.6584	3.090	—0.008	—0.004	3.078	1.8560	—0.04

Average rise per gram benzoic acid (weighed in air) = 1.8567°.
Average rise per gram benzoic acid (weighed in vacuum) = 1.8552°.

effect of the changing heat capacity of water is at least partially neutralized.

The internal agreement of the two series on sugar and benzoic acid indicates that the new bomb can be safely used for work involving the highest accuracy. The greatest deviation from the mean is 7 parts per 10,000 in the case of sugar and 4 parts per 10,000 in the case of benzoic acid. This is probably as close an agreement as can be expected from a mercury thermometer and, indeed, it compares very favorably with the best work with electrical thermometers.

The results described in this paper are not absolute, but are purely relative. Therefore, it is interesting to compare the ratio of sugar and benzoic acid. The ratio resulting from this series (vacuum weights) is 1.6014. A similar comparison of a very high order of accuracy has been made by Emil Fischer and Wrede.[1] They have made two series of determinations on benzoic acid. The ratio from their first and most concordant series is $\frac{26.478\text{Kj}}{16.545\text{Kj}} = 1.6003$; that from the average of the two series is $\frac{26.472}{16.545} = 1.6000$; while the ratio from their three highest determinations of benzoic acid is 1.6008. The differences between these ratios and that found in this paper are respectively 0.07 per cent., 0.09 per cent., and 0.035 per cent. The value of the ratio found by the Bureau of Standards is 1.6016.[1] The agreement here is even more satisfactory; in fact, it is identical within the possible experimental accuracy. In spite of the concordance of their ratios the absolute values assigned by Fischer and Wrede and the Bureau differ by a quarter of a per cent. The reason for this discrepancy is not apparent at present.

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[1] *Sitzber. K. Acad. Berlin*, **19, 20, 21,** 687 (1904); *Z. physik. Chem.*, **53,** 161 (1903); **69,** 218 (1909); **75,** 81 (1910).

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[1] Private communication from Dr. W. F. Hillebrand.

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